Cryogenic Fluids or Cryogens

Los Alamos National Laboratory
Laboratory Implementation Requirements LIR402-580-01.2
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1.0 Introduction

Note: *Click here* for Lessons Learned that may apply to the requirements contained in this LIR.

1.1 Overview

The Laboratory requires that cryogenic fluids (cryogens) shall be controlled through operational evaluations and hazard control measures to ensure the safety of Laboratory personnel. Cryogenic fluids used at the Laboratory include but are not limited to liquid nitrogen, liquid helium, liquid argon, liquid oxygen, and liquid hydrogen. This LIR complements LPR 402-00-00, "Worker Health and Safety," Appendix 18, "Pressure/Cryogens." The requirements in this document shall become effective immediately on the issue date. Design, use, and maintenance of cryogenic systems are addressed in LIR 402-1200-01, "Pressure, Vacuum, and Cryogenic Systems."

The four principal hazards of cryogens are displacement of oxygen, freezing of eyes and skin, explosions due to pressure build-up, and breakage of glass Dewars. Further information on hazards, including the hazards of phase changes, can be found in Attachment A, "Technical Guide to Cryogens."

1.2 In This Document

2.0 Purpose

The purpose of this LIR shall be

- to identify the hazards of these materials and establish effective controls,
- to identify the materials that are subject to these requirements, and
- to establish the implementation requirements for controlling the use of cryogens at the Laboratory.

3.0 Scope and Applicability

All Laboratory organizations involved in operations that use cryogens shall be subject to the requirements contained in this document. This document shall apply to all Laboratory workers, including employees, affiliates, and visitors who may be exposed to cryogens in the course of their work. This document shall apply to vendors, contractors, subcontractors, and their employees to the degree specified in their contract.

Cryogenic systems or Dewars equipped with a pressure relief system set above 15 psig shall be considered to be pressurized systems; the requirements of LIR 402-1200-01, "Pressure, Vacuum, and Cryogenic Systems," shall also apply.

4.0 Definitions

4.1 Acronyms and Abbreviations

AR	Administrative requirement
C&LGSC	Cryogenic and Liquefied Gas Safety Committee
CFR	Code of Federal Regulations
HSR	Health, Safety, and Radiation Protection Division
HSR-2	Occupational Medicine Group
HSR-5	Industrial Hygiene and Safety Group
PS-13	ES&H Training Group
IMP	Implementation Procedure
IWD	Integrated Work Document
LIR	Laboratory implementation requirement
MSDS	Material safety data sheet
PPE	Personal protective equipment
psi/psig	Pounds per square inch/pounds per square inch gauge
SUP-5	Packaging and Transportation
V_s	Safe amount of cryogen (see Section 5.5.1)

4.2 Terms

Adequate ventilation—Adequate ventilation is considered to occur when room air is totally replaced with fresh air at least once every 10 minutes (6 air changes per hour).

Asphyxiant—A gas whose primary or most acute health effect is asphyxiation or suffocation resulting from lack of oxygen. There are two classes of asphyxiant: simple asphyxiants, which act by displacing oxygen, and chemical asphyxiants, which cause asphyxiation by preventing oxygen uptake at the cellular level.

Cryogenic and Liquefied Gas Safety Committee—A Laboratory committee that provides a source of independent peer review at the Laboratory, providing advice and counsel to Laboratory groups and individuals on safe use of cryogenic and liquefied gases.

Cryogenic fluid (cryogen)—A liquid with a normal (i.e., at standard temperature and pressure) boiling point below approximately 120 K (-238^{o}F, -150^{o}C) that can be used as a working fluid in mechanical refrigerators or as a cooling bath in cryostats. See also the definition for inert cryogen.

> **Guidance Note**: The cold vapor of solid carbon dioxide (sublimation temperature at 1 atm: 195 K, -83^{o}F, -78^{o}C) can be considered a cryogenic fluid.

Cryogenic system—A system operating at temperatures where cryogenic fluids could be condensed or containing cryogenic fluids at or near normal boiling point temperatures. Add the second sentence.

Dewar—A thermally insulated, vented vessel designed to contain cryogens for long periods.

Employee—Any Laboratory worker, including affiliates, visitors, vendors, contractors, subcontractors, and their employees, who may be exposed to cryogens under normal operating conditions.

Expansion ratio—The amount of gas (in liters) formed when 1 L of a liquid cryogen is warmed from the normal boiling point to room temperature while maintaining the pressure at 1 atm.

Hazard control measures—A hierarchy of controls that includes engineering controls, administrative controls, or PPE to mitigate workplace hazards.

Integrated Work Document – A worker-friendly document that describes the work activity, identifies the hazards and links them to specific controls. The IWD may be a subset of a larger work package that includes other documents and information that do not address hazards and controls for that activity. See IMP 300, "Integrated Work Management for Work Activities."

Qualified industrial hygienist—A person who is certified in the practice of industrial hygiene or who meets the American Board of Industrial Hygiene eligibility requirements for certification *and* has required working knowledge, training, and/or experience in supporting activities involving ventilation controls and cryogen hazards.

Inert cryogen—The cryogenic condensed phase of either a noble gas (helium-3, helium-4, neon, argon, or krypton) or nitrogen. These cryogens are inert because of their low chemical activity. Inert cryogens are simple asphyxiants. All other cryogens are considered noninert.

Material safety data sheet—Written or printed material concerning a hazardous chemical, which is prepared in accordance with 29 CFR 1910.1200(g).

Normal oxygen content—Air with 21% oxygen content by volume.

Oxygen deficiency—Refers to air with less than 19.5% oxygen content by volume.

Oxygen enrichment—Refers to air with more than 23.5% oxygen content by volume.

Trapped volume—Any element of a piping/vessel system, typically between two valves, that does not have a relief valve or rupture disk.

> **Guidance Note:** The pressure in a trapped or constant volume that is completely filled with liquid nitrogen can reach approximately 45,000 psi when warmed to room temperature.

5.0 Implementation Requirements

5.1 Overall Responsibility

Unless otherwise stated in this document, the responsible line manager shall ensure that the requirements specified herein are met.

5.2 Specific Responsibilities

Individual or Organization	shall
Associate Director for Technical Service	▪ charter and authorize the C&LGSC.
Responsible Division	• be responsible for assigned facilities and processes and for

Leader	activities associated with cryogens in those facilities and processes.
Responsible Line Managers	▪ be responsible for cryogenic vessels and systems that are group, program, or facility property. ▪ review and approve all applicable IWDs that involve cryogens and ensure that the IWDs are understood and implemented. ▪ ensure that Laboratory designed systems that contain or utilize cryogens are designed according to good engineering practices. Guidance Note: The C&LGSC is available for reviewing design documentation. ▪ ensure that new Dewars and piping are inspected before use and on a regular basis. ▪ ensure that large cryogenic systems and associated engineering controls, such as ventilation systems and pressure relief valves, are maintained. ▪ ensure that sensors or monitors for cryogens are calibrated and maintained in accordance with the manufacturer's instructions. ▪ ensure that all cryogen work performed by members of the group has been identified and that through training, experience, and working knowledge the workers are authorized to work with cryogens. ▪ ensure that all work under their supervision complies with this LIR. ▪ correct any identified deficiencies.
	▪
Cryogenic and Liquefied Gas Safety Committee, upon request	▪ review drawings, sketches and calculations provided by Responsible Line Managers. ▪ use the expertise of committee members to assist Laboratory cryogen users in identifying and evaluating hazards and in developing and evaluating controls associated with cryogens or liquefied gas. ▪ review existing and proposed cryogenic systems and cryogenic liquids or liquefied gas operations at the Laboratory using available safety and engineering data upon request. ▪ review the storage systems (e.g., Dewars) for cryogenic liquids using available safety and engineering data upon request. ▪ assist with developing and reviewing this LIR, and IWDs for cryogenic systems, cryogenic liquids, and liquefied gas operations.
Laboratory Cryogen Users	▪ coordinate the development of the IWDs for cryogen operations. ▪ for inert cryogens, - determine the amount of cryogen used or stored in the specific operation, - calculate the safe amount for the cryogen (see Section 5.5.1), - obtain an evaluation from a qualified industrial

	hygienist as to whether adequate ventilation is available for the work area and/or additional controls are required. ▪ when carbon monoxide is used or stored, ensure that carbon monoxide sensors or monitors are used. ▪ obtain a qualified industrial hygienist review of new operations or significant changes in existing operations when - neither adequate ventilation, nor oxygen sensors, nor ventilation failure monitors are present in the workplace or - the amount of cryogen used or stored is greater than 30 * V_s . - ▪ ensure that only authorized personnel perform cryogen operations. ▪ maintain a file of documentation relevant to the cryogen operation (e.g., designs, C&LGSC reviews, qualified industrial hygienist evaluations,IWD). ▪ ensure that all cryogen work complies with this LIR. ▪ be familiar with the requirements for adequate ventilation for the work area and the volume of cryogen that can be safely used. ▪ understand the hazards associated with the cryogen use. ▪ follow the IWD for the cryogen operation. ▪ be familiar with emergency response procedures.
Qualified Industrial Hygienist	▪ assist organizations in determining the hazards and appropriate control measures for cryogenic operations. ▪ conduct periodic surveys of cryogen operations and provide results and recommendations to safety-and-environmentally-responsible line managers/supervisors. ▪ evaluate as to whether adequate ventilation is available for the work area and/or additional controls are required in areas where inert cryogens are used, identify monitor requirements and placement, and determine actions if the V_s for an inert cryogen is exceeded. Document and retain the evaluation for inspection and review. ▪ review new operations or significant changes in existing operations when - neither adequate ventilation, nor oxygen sensors, nor ventilation failure monitors are present in the workplace or - the amount of cryogen used or stored is greater than 30 * V_s . Document and retain the evaluation for inspection and review. .
Industrial Hygiene and Safety Group (HSR-5)	▪ provide toxicity and ventilation requirements to Laboratory employees upon request. ▪ provide consultations about necessary procedures and precautions when working with cryogens.

	▪ coordinate issues of cryogenic safety with the C&LGSC. ▪ perform quality assurance checks of calibration and maintenance records for sensors or monitors used in cryogen areas (e.g., oxygen and carbon monoxide) and provide results and recommendations to safety and environment responsible line managers/supervisors.
Occupational Medicine Group (HSR-2)	▪ provide a consultation and a medical examination whenever an employee develops signs or symptoms that indicate potential exposure to a cryogenic fluid.
ES&H Training Group (PS-13)	▪ develop and implement ES&H training for cryogen use. ▪ assist organizations in providing training.
Packaging and Transportation (SUP-5)	▪ be responsible for cryogen purchase and delivery. ▪ maintain and inspect portable liquid helium storage Dewars.

5.3 General Requirements

A qualified industrial hygienist shall evaluate proposed operations when

- neither adequate ventilation, nor oxygen sensors, nor ventilation failure monitors are present in the workplace or
- the amount of cryogen used or stored is greater than 30 * V_s .

> **Guidance Note**: 30 * V_s is based on 6 air changes per hour.

A qualified industrial hygienist shall be consulted to determine whether adequate ventilation exists, to identify monitor requirements and placement, and to determine actions if the V_s for an inert cryogen is exceeded (see Section 5.5.1). The evaluation shall be conducted before the operation begins. The safety-and-environmentally-responsible line manager/supervisor owning air-monitoring equipment shall have a written procedure that describes use, calibration, maintenance, alarm response procedures, and reentry procedures.

> **Guidance Note:** A qualified industrial hygienist can assist in preparing written procedures. The written procedure may be part of anIWD. To minimize operational delays, the evaluation should take place during the initial planning stages to allow time for purchasing air-monitoring equipment and for designing control systems.

5.4 Controls

5.4.1 General Controls for All Cryogens

The hierarchy of controls as stated in LPR 402-00-00, “Worker Health and Safety,” shall be followed. Based upon the work, specific controls shall be:

Type	Control
Engineering	▪ Ventilation systems. ▪ Orifices to reduce flow rates. ▪ Use of caps or seals to prevent condensation of air into Dewars. ▪ Venting to a safe outdoor location or assurance of adequate ventilation for vacuum-jacketed tanks. ▪ Dust caps for liquid transfer hoses. ▪ Relief valves and, if required, frangible discs, to eliminate trapped volumes. ▪ Wrap glass Dewars in tape or enclose in a protective housing. ▪ Authorized storage locations with signs, barriers, demarcation, dispersion, monitors, and availability of appropriate PPE. ▪ Installation of monitors audible to an employee entering the room, such as oxygen sensors, ventilation failure monitors, flammable gas monitors, or monitors specific to the cryogen, e.g., carbon monoxide.
Administrative	▪ Post the hazards and label the contents of the cryogen in accordance with specified requirements. ▪ Prepare anIWD. ▪ Develop procedures for properly handling and filling transfer vessels. ▪ Provide oxygen and combustible-gas sensors or monitors. ▪ Label all cryogen-handling systems with the contents and ensure that required pressure gauges and pressure relief valves are in place so that high pressures cannot build up in lines or in Dewars. ▪ Store Dewars only in approved locations. **Guidance Note:** ▪ Avoid dropping solids or liquids into cryogenic liquids. ▪ Avoid breathing vapors from a liquid cryogen source. ▪ When discharging cryogens, open valves slowly to avoid splashing. ▪ Stand clear of boiling or splashing liquid and its vapors when opening vents until pressure has equalized. ▪ When recharging or filling Dewars, return to the Dewar at the anticipated time of recharge or fill completion and monitor for O_2 if deemed necessary by a qualified industrial hygienist. ▪ Take particular caution when working with cryogens in glass Dewars. ▪ Gradually precool Dewars before filling to avoid thermal shock and reduce excessive flashing and loss of product. ▪ Take care to prevent air from diffusing down the neck of a Dewar, which can cause blockage. ▪ Maintain Dewars at a positive pressure relative to the surrounding atmosphere. ▪ Slowly vent Dewar boil-off to warmer zones.

<table>
<tr><th>Type</th><th>Control</th></tr>
<tr><td>Personal Protective Equipment</td><td>Employees shall

▪ wear eye protection when handling cryogens.
▪ wear a face shield and eye protection when transferring a cryogen from a storage vessel of cryogen at pressures higher than 7 psig into an open Dewar.

Guidance Note: Typical pressures in 100-L helium Dewars range from 1 to 3 psig as received. Typical pressures in 160- to 230-L nitrogen Dewars range from 20 to 30 psig as received.

Guidance Note:

- Wear footwear made of impermeable materials; open-toe footwear is discouraged when handling cryogens.
- Wear loose-fitting, long-sleeved protective clothing, long pants with no cuffs (left outside of footwear), and loose-fitting, insulated gloves.

In addition, employees shall

▪ use self-contained breathing apparatus and rescue equipment when responding to an emergency response associated with the use of a cryogen when oxygen-deficient or enriched conditions could exist.</td></tr>
</table>

5.4.2 Additional Controls for Oxygen shall be:

<table>
<tr><th>Type</th><th>Control</th></tr>
<tr><td>Engineering</td><td>▪ Use only approved lubricants with oxygen equipment.</td></tr>
<tr><td>Administrative</td><td>▪ Keep all combustible materials, especially oil or grease, away from oxygen.
▪ Do not permit smoking or open flames in any area where liquid oxygen is used or stored.
▪ Post “no smoking” signs.
▪ Do not permit oxygen to come in contact with organic or flammable materials. If liquid oxygen spills onto asphalt or other surfaces contaminated with combustibles, e.g., oil-soaked concrete or gravel, do not walk on or roll equipment over the area of the spill. Keep sources of ignition away for at least 30 min after all frost or fog has disappeared.
▪ Operate valves in oxygen service slowly to avoid ignition of any contaminants that might be in the system.
▪ Remove clothing that has been splashed or soaked with liquid oxygen immediately and air until frost or fog has disappeared.
▪ Purge oxygen equipment with air before performing maintenance.</td></tr>
</table>

5.4.3 Additional Controls for Flammable Cryogens (including, but not limited to hydrogen) shall be:

Type	Control
Engineering	▪ Ground electrical equipment. ▪ When transferring liquid hydrogen from one system to another, electrically connect both systems and the transfer tube(s) to a common ground. ▪ Provide adequate ventilation as defined in Section 4.2. ▪ Pipe flash-off gas from a closed liquid hydrogen container to a laboratory hood vented outside the building or vent by other means to a safe location. The design of new hydrogen ventilation systems shall ensure that the ductwork is independent of other systems and that sources of ignition are eliminated at the exhaust system outlet. ▪ Use intrinsically safe electrical equipment including motors, if needed. **Guidance Note**: Equip hydrogen ventilation systems with an inert gas (nitrogen) purge capability to prevent ignition of hydrogen and air mixtures at the start of venting.
Administrative	▪ Do not permit smoking or open flames in areas where flammable cryogenic liquids are used or stored. ▪ Post “no smoking” signs in areas where flammable cryogenic liquids are used or stored. ▪ Wear work clothes that minimize ignition sources, such as static electricity, in atmospheres possibly containing hazardous concentrations of flammable cryogens.

5.4.4 Additional Controls for Carbon Monoxide shall be:

Type	Control
Administrative	▪ Use an inert cryogen to test and purge vessels, pipelines, vaporizers, and controls at pressures and temperatures near actual operating conditions. ▪ Always assign at least two workers to operations in which carbon monoxide is used or stored. ▪ Install a carbon monoxide sensor or monitor.

5.5 Adequate Ventilation

The cryogen user shall have documented knowledge of adequate ventilation through design evaluation and/or measurement, and shall obtain such information from a qualified industrial hygienist. The industrial hygienist shall coordinate with the facility manager or building manager to obtain any additional required information on ventilation systems. Areas (such as clean rooms) in which air is recirculated through particulate filters shall not qualify as having adequate ventilation for cryogen use. **Guidance Note:** An inert cryogen decision flow chart is provided at the end of Attachment A.

5.5.1 Safe Amount for Inert Cryogens

Users of inert cryogens shall determine, with assistance when requested from a qualified industrial hygienist, what amount of inert cryogen may be used safely in a work space by (1) determining the volume of the work space, V_w, in cubic meters (room volumes should be corrected for equipment occupying the room) and (2) using the following equation to calculate the safe volume, V_s, of inert cryogen (in liters of liquid):

$$V_s^* = V_w/14 \ .$$

> **Guidance Note**: *Amounts larger than V_s may be safely used when adequate ventilation is present in the workspace.

The presence of adequate ventilation shall be determined as described in this section.

> **Guidance Note**: This calculation is conservative; no supply or exhaust ventilation is assumed. The calculation is based on ensuring a level of oxygen of at least 19.5%.

> **Guidance Note**: At Los Alamos (where normal atmospheric pressure is approximately 580 torr), 1 L of liquid nitrogen boiling at 75 K generates 0.93 m^3 of gas at room temperature. Because other cryogens have similar expansion ratios, assuming that 1 L of *any* liquid cryogen generates about 1 m^3 of gas at room temperature is a good approximation.

> **Guidance Note**: Users of inert cryogens should obtain assistance from a qualified industrial hygienist in determining what amount of inert cryogen may be used safely in a work space.

5.5.2 Confined Spaces

Cryogen users shall ensure that only the volume of the confined space itself is used to calculate V_w. For other requirements, see LIR 402-810-01, "Confined Spaces."

5.6 Training and Qualifications

Before employees work with cryogens, responsible line managers shall ensure that training is provided that addresses

- information on the nature and properties of the cryogens in both the liquid and gaseous phase and for CO_2 in the solid phase,
- specific instructions on the equipment to be used,
- hazards of a particular cryogen,
- hazard control measures,
- IWDs and MSDSs,
- approved materials that are compatible with the cryogenic liquid,
- use and care of protective equipment and clothing, and
- emergency response procedures.

> **Guidance Note**: PS-13 offers a training course called Cryogen Safety Awareness.

5.7 Emergency Response

Written emergency response procedures shall be made part of the IWD for cryogenic operations. Emergency response personnel who are called to areas where cryogenic operations are performed and where inadequate ventilation may have resulted in oxygen deficiency shall wear self-contained breathing apparatus and other required rescue equipment. Other specific emergency response requirements shall be as detailed in the table below.

If . . .	**then . . .**
A water or air ice plug occurs in a Dewar	**A trained 2-person team shall attempt to unplug it with a warm copper rod or tube if that activity can be performed safely. If the Dewar can not be unplugged safely, call EM&R at 7-6211. Required procedures shall always be implemented to ensure minimization of the risk of such plugging.**
a cryogen spill occurs **AND** an oxygen monitor is absent, and the status of the ventilation system or the amount of cryogen is unknown,	evacuate the work space until the ventilation system has had sufficient time to refresh the air supply, which may be verified by testing the work space with a portable oxygen monitor.
a qualified industrial hygienist determines that engineering controls are inadequate for such operations,	emergency procedures shall be posted at the entrance to the work area.

5.8 Accident and Incident Reporting

Accidents and incidents shall be reported as soon as possible to the responsible line manager. Associated injuries and illnesses shall be reported to the Occupational Medicine Group (HSR-2). The responsible line manager shall participate in identifying the causes and implement corrective actions to prevent recurrence. See LIR 402-130-01, Abnormal Events.

6.0 References

Compressed Gas Association 1987. “Safe Handling of Cryogenic Liquids,” Pamphlet P-12.

Department of Energy, “Pressure Safety Requirements,” DOE Order 440.1, Attachment 1, Paragraph 6.

Department of Transportation. “Transportation,” Title 49, Code of Federal Regulations.

Edeskuty, F. J., and W. F. Stewart, 1996. Safety in the Handling of Cryogenic Fluids, Plenum Press, New York, New York.

Haselden, G. G., 1971. Cryogenic Fundamentals, Academic Press, New York, New York.

Los Alamos National Laboratory document LIR 402-130-01, “Abnormal Events.”

Los Alamos National Laboratory document LIR 402-510-01, “Chemical Management.”

Los Alamos National Laboratory. document LIR 402-810-01 “Confined Spaces.”

Los Alamos National Laboratory document, IMP300, “Integrated Work Management.”

Occupational Safety and Health Administration. “Hazardous Materials,” Title 29, Code of Federal Regulations, Part 1910.101–1910.120.

Williamson, K. D., and F. J. Edeskuty, 1983. Liquid Cryogens, Vols. I and II, CRC Press, Boca Raton, Florida.

Zabetakis, M. G., 1987. Safety with Cryogenic Fluids, Plenum Press, New York, New York.

6.2.2 Required Records

- The Laboratory user group shall keep records of all qualified industrial hygienist and C&LGSC reviews, maintenance, and inspections of their cryogenic operations. Copies of the IWD shall be kept on file.
- PS-13 and the cryogen user group shall maintain training records.
- Responsible line managers shall maintain records documenting regular maintenance and calibration of air-monitoring equipment.

7.0 Attachments

Attachment A Technical Guide to Cryogens

ATTACHMENT A

TECHNICAL GUIDE TO CRYOGENS

Guidance

1.0 General Hazards

A typical cryogen becomes a gas at ambient temperature and atmospheric pressure. Cryogens include but are not limited to argon (87 K, -303°F, -186°C), helium-3 (3.2 K, -428°F, -270°C), helium-4 (4.2 K, -427°F, -269°C), hydrogen (20 K, -423°F, -253°C), krypton (120 K, -244°F, -153°C), neon (27 K, -411°F, -246°C), nitrogen (77 K, -320°F, -196°C), and oxygen (90 K, -297°F, -183°C) (normal boiling point temperatures in parentheses). Liquefied natural gas, liquid methane (112 K, -259°F, -161°C), and carbon monoxide (81 K, -313°F, -192°C) are also handled as cryogenic liquids. Most cryogens are odorless, colorless, and tasteless when vaporized to the gaseous state. Cold boil-off gases condense the moisture in the air, creating a highly visible fog that normally extends over a larger area than the vaporizing gas. Personnel working with cryogens are potentially exposed to the following hazards/effects:

- skin or eye contact with extremely cold cryogenic liquid and boil-off vapors, resulting in frostbite or burns,
- contact with broken glass from Dewars,
- simple (i.e., inert cryogens) or chemical (i.e., carbon monoxide) asphyxiation from an oxygen-deficient atmosphere (applies to all cryogens except oxygen),
- explosion caused by
  - evaporation and pressure buildup of cryogens in confined geometries or
  - accumulation of liquid oxygen condensed from the surrounding air,
- ignition of flammable cryogens (including carbon monoxide, natural gas, and liquid hydrogen), and
- acute respiratory problems.

2.0 Specific Hazards

2.1 Inert Cryogens

The principal hazards associated with inert cryogens and with carbon dioxide (dry ice) are asphyxiation and burns.

2.2 Oxygen

Oxygen is nonflammable, but it vigorously accelerates and supports combustion. Substances that burn in air burn much more vigorously in oxygen. Release of liquid oxygen may result in an oxygen-enriched atmosphere, which lowers ignition temperatures and causes rapid combustion. Generally, the upper flammable limit for a flammable gas in air is raised in oxygen-enriched atmospheres, which means that fire or explosion becomes possible over a wider range of gas mixtures.

Liquid oxygen with fuels, oils, and/or grease may form mixtures that are shock-sensitive. Solids such as asphalt or wood that have a porous structure can become saturated with oxygen and detonate when shocked. Ignition is more likely to occur with weaker sparks and lower temperatures than would be the case in air.

2.3 Carbon Monoxide

Carbon monoxide presents all the hazards described in Section 1, as well as the additional hazards of high toxicity and flammability. Carbon monoxide combines with the hemoglobin of red blood cells to form carboxyhemoglobin, which prevents hemoglobin from taking up oxygen. Carbon monoxide is also a flammable gas.

2.4 Flammable Cryogens

Flammable cryogens include hydrogen, liquefied natural gas, liquid methane, and carbon monoxide. The principal hazards associated with these cryogens are fire and explosion.

3.0 Oxygen Deficiency

Because the liquid-to-gas expansion ratio of cryogens is approximately 1,000 when used at the Laboratory (elevations between 7,000 and 8,000 ft), an oxygen-deficient atmosphere (air with less than 19.5% oxygen content by volume) can result from a release or spill of cryogens, which then evaporates to a gas at room temperature. Most cryogens used at the Laboratory can produce an oxygen-deficient atmosphere.

Particular hazards can exist when cryogens are used near floor pits or other low areas because the cold vapors from evaporating cryogens may accumulate in low areas. Thus, areas not conventionally classified as confined spaces may need to be treated as such when cryogens are present (see LIR 402-810-01, “Confined Spaces,” for confined space requirements).

4.0 Frostbite

In general, frostbite occurs in tissue only after prolonged exposure to temperatures below 0°C. At such temperatures, local blood circulation stops, possibly resulting in tissue damage. Because blood delivers heat to the affected part, the amount of heat removed from the tissue and the rate at which it is removed determine the extent of frostbite.

Frostbite without pain may occur from direct contact with either a cryogenic liquid or a cryogenically cooled solid, such as metal. If frostbite occurs (the skin appears white), the following precautions should be taken:

- Thaw the frozen tissue rapidly, usually with body-temperature water.

  Note: Small frozen white spots on the fingertips can be thawed immediately in your mouth.

- Never rub frozen tissue.
- During working hours (8 a.m. to 5 p.m.), the Occupational Medicine Group (HSR-2) shall be contacted for medical attention.
- After working hours (5 p.m. to 8 a.m.), contact the Los Alamos Medical Center.

5.0 Eye Damage

Because the eye is constantly lubricated by water, the surface of the eye freezes faster than does bare skin. A splatter of small droplets of cryogenic fluid may either bounce off or just blister the skin. Wear eye protection when transferring cryogens from Dewars. Frostbite of the eye can result in losing the eye lens.

6.0 Respiratory Disorders

Certain cryogens present respiratory hazards other than the serious hazard of asphyxiation from oxygen depletion. **Examples:**

- Carbon dioxide can affect the body's breathing rate because of its role in respiration.
- All noble gases (especially xenon and argon) have an anesthetic or narcotic effect that can diminish the symptoms of hypoxia, such as air hunger, and can markedly decrease the ability to self-rescue.

7.0 Physical Hazards

The significant temperature difference between cryogens and the surrounding environment can result in the following phenomena:

- large energy transfers,
- high pressures,
- changes in material properties, and
- temperature gradients with thermal and mechanical stresses.

8.0 Phase Changes

8.1 Heat

Compared with the gas phase at ambient temperature and atmospheric pressure, liquid cryogens are very dense. Heating to the gas phase a cryogenic fluid that is trapped in a fixed volume can result in very high pressures. Regardless of how expertly a Dewar or vacuum-jacketed cryogenic line is constructed, some ambient heat always reaches the cryogenic liquid. **Example**: Liquid nitrogen trapped in a fixed or constant volume can reach 45,000 psi in a period of time that depends on the rate of the heat leak.

8.2 Flash Vaporization

If heat input into a cryogen is excessive, flash vaporization may occur with an explosive rapidity known as a "boiling liquid, expanding vapor explosion" (BLEVE).

> **Note**: Such a condition frequently occurs after spills or when pressure on a saturated liquid at an elevated boiling point is suddenly released (by a ruptured disc or by a ruptured line or Dewar, for example).

8.3 Pressure

Typical pressures in 100-L helium Dewars range from 1 to 3 psig, as received. The typical pressures of the relief valves in new, factory-equipped, 160- to 250-L Dewars are set above 200 psi, and the pressures of the rupture discs are set even higher. For safe usage, the pressure should be in the range of 20 to 30 psig, which requires an additional pressure relief valve set in this pressure range.

9.0 Low-Temperature Effects

Many materials, such as carbon steel, become brittle at low temperatures. Because the properties of most materials are altered at decreased temperatures, one should evaluate the effects of cryogens on structural and other materials when designing a cryogenic system. Tensile and impact strength data should also be evaluated when choosing materials for such systems.

10.0 Structural Failure

Structural failure may result from thermal stresses caused by the following physical effects:

- a temperature differential across a material,
- bonding of materials having unlike expansion coefficients, and
- use of a material whose length remains constant during a change in temperature.

For long, stainless-steel pipelines, approximately 1/16 in./ft should be allowed for shrinkage. This detail should be considered very important for vacuum-jacketed lines because the outer enclosure remains at ambient temperature.

In addition, the following materials characteristics should be kept in mind:

- Materials suitable for low-temperature service, such as the 300-series stainless steels, should be used in cryogenic systems.
- Materials embrittled by hydrogen should not be used in a hydrogen system.
- Stabilized austenitic stainless steels (316, 321, and 347), phosphor bronze, and beryllium copper are satisfactory for hydrogen service at elevated pressures.

11.0 Ice Buildup

Because moisture from the surrounding air condenses on cold surfaces, critical elements, such as pressure relief valves and valve packings, should either be kept above freezing temperature or shielded.

Vent lines are often used to eliminate trapped volumes. Removing cryogenic fluids or causing other pressure fluctuations can move air into the vent line. The water carried in humid air can freeze out and plug the line, which can result in the high-pressure buildups noted above. Vent lines should be designed to prevent this problem.

12.0 Chemical and Reactive Hazards

Some cryogens react violently when combined with each other or with their surroundings. Fire and explosion hazards can result when oxidizers (air, oxygen, fluorine, nitric oxide, or ozone) are combined with various combustibles or flammables (methane, hydrogen, or construction materials).

Because the condensation temperature of oxygen is higher than that of most other cryogens, liquid oxygen can form in unexpected locations.

- If air is allowed to flow through a liquid nitrogen trap that is used to remove organic vapors, the trap also removes oxygen. Mixing organic vapors with oxygen can produce explosive combinations.
- Oxygen tends to condense to a liquid on surfaces at liquid nitrogen or liquid air temperatures. A shiny, shimmering surface may indicate the presence of liquid oxygen. Another indicator that liquid oxygen is present is its light blue color. This color may not be observable, depending on the quantity of liquid oxygen, available light, and colors of surrounding materials. Therefore, it is important to remember that the absence of the light blue color does not rule out the presence of liquid oxygen. However, the light blue color is a very good indicator of liquid oxygen presence when observed. Take precautions to eliminate this hazard.

13.0 Dewar Flasks

Dewar flasks are portable containers for cryogenic liquids. For helium Dewars, care should be taken to prevent air from diffusing down the neck of the flask and producing a plug of solid air. In Dewar flasks containing liquid nitrogen or oxygen, ice (solid water) is the chief agent that can cause blockage and thus a slow but continuous pressure increase in the Dewar, which may eventually result in violent failure.

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